Stable oil-in-water emulsion, process for manufacturing it and its use in cosmetics and dermatology

The invention relates to a stable oil-in-water (O/W) emulsion comprising oil globules with an average size of less than 20 microns and containing at least 15% of oily phase and at least one copolymer of a fatty-chain carboxylic acid. The invention also relates to the process for preparing such an emulsion and to its use in cosmetics and/or dermatology.

For various reasons associated in particular with their substantial feeling of comfort when used and their freshness, cosmetic compositions are usually in the form of an emulsion of the oil-in-water type, comprising an oily phase uniformly dispersed in an aqueous phase. In these conventional emulsions, the size of the globules constituting the fatty phase is generally greater than several tens of microns. Such emulsions can have cosmetic properties (oily feel) and physical properties (stability) that are insufficient. The insufficiency of stability is reflected by the appearance of a phenomenon of separation (dephasing) between the aqueous and oily phases of the emulsion. This instability is detrimental to the storage of the emulsions.

In order to obtain a stable emulsion, it is necessary to add emulsifiers (or surfactants) thereto, which place themselves at the interface of the aqueous and oily phases. However, the presence of surfactants has several drawbacks, and in particular it usually requires the emulsion to be prepared under warm

conditions, which especially limits the nature of the active agents to be introduced into the emulsion. In particular, this process excludes the use of heat-sensitive active agents. Thus, it has been sought to dispense with surfactants. Moreover, surfactants can lead to irritations, in particular in individuals with sensitive skin.

The Applicant Company has discovered, unexpectedly, that emulsions with a large content of oily phase and free of surfactant can be prepared by having globules of oil with an average size of less than 20 microns and by using a copolymer consisting of a major fraction of monoolefinically unsaturated C_3-C_6 carboxylic acid monomer or its anhydride and a minor fraction of acrylic acid fatty-chain ester monomer.

A subject of the present invention is thus an emulsion comprising an oily phase dispersed in an aqueous phase, characterized in that the globules of the oily phase have an average size of less than 20 microns, in that the oily phase constitutes at least 15% by weight relative to the total weight of the emulsion and in that the aqueous phase contains at least one copolymer consisting of a major fraction of monoolefinically unsaturated C_3-C_6 carboxylic acid monomer or its anhydride and a minor fraction of acrylic acid fatty-chain ester monomer, and in that it is free of surfactant.

Admittedly, it is known practice to use fatty-chain polymers to stabilize an emulsion, but when the amount of oil is too large, the emulsion has a tendency to become destabilized over time. According to the present invention, good stability is obtained even in the presence of a large amount of oil, due to the fact that the oil globules are sufficiently small in size. In addition, these oil globules are monodispersed, i.e. they virtually all have the same size, unlike the emulsions of the prior art in which the particles of dispersed phase usually have quite diverse sizes.

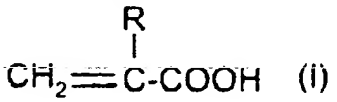
The copolymers used in the emulsion of the invention have the advantage, over the surfactants usually used, not only of stabilizing the emulsion but also of gelling it. In addition, unlike surfactants, they do not penetrate into the skin, thereby considerably reducing the risk of irritation.

The copolymers used in the emulsions in accordance with the present invention are prepared by polymerizing a predominant amount of monoolefinically unsaturated carboxylic acid monomer or its anhydride, with a smaller amount of an acrylic fatty-chain ester monomer. The term "fatty chain" means a linear or branched alkyl radical containing from 8 to 30 carbon atoms.

The amount of carboxylic acid monomer or of its anhydride preferably ranges from 80 to 98% by

weight and more particularly from 90 to 98% by weight, whereas the acrylic ester is present in amounts ranging from 2 to 20% by weight and more particularly from 1 to 10% by weight, the percentages being calculated relative to the total weight of the two monomers.

The preferred carboxylic monomers are chosen from those corresponding to formula (I) below:

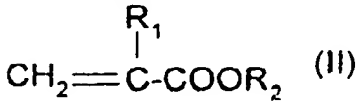


(I)

in which R denotes hydrogen, a halogen, a hydroxyl group, a lactone group, a lactam group, a cyanogen (-C=N) group, a monovalent alkyl group, an aryl group, an alkylaryl group, an aralkyl group or a cycloaliphatic group.

The carboxylic monomers which are particularly preferred are chosen from acrylic acid and methacrylic acid or mixtures thereof.

The acrylic fatty-chain ester monomers are preferably chosen from those corresponding to formula (II) below:



(II)

in which R_1 is chosen from the group formed from hydrogen, a methyl radical and an ethyl radical, and R_2 is a C_8-C_{30} alkyl group.

The ester monomers which are particularly preferred are those for which R_1 is hydrogen or a methyl radical and R_2 is a C_{10}-C_{22} alkyl group.

The copolymer used in the emulsion of the invention can optionally be crosslinked using a crosslinking agent used in an amount ranging from 0.1 to 4%, preferably from 0.2 to 1%, by weight relative to the total weight of carboxylic monomers and of acrylic ester monomers. The crosslinking agent can be chosen in particular from polymerizable monomers containing a polymerizable CH_2=C- group and at least one other polymerizable group, in which the unsaturated bonds are not conjugated with each other.

These copolymers are described in document EP-A-0 268 164 and are obtained according to the preparation methods described in that same document.

The copolymers more particularly used are those with a viscosity, measured using a Brookfield viscometer in an aqueous 2% solution and at 25°C, of less than or equal to 5000 cPs (5 Pa.s) and more preferably of about 3000 cPs (3 Pa.s), and more especially acrylate/C_{10}-C_{30}-alkylacrylate copolymers such as the products sold under the names Pemulen TR1, Pemulen TR2 and Carbopol 1382 by the company Goodrich, or mixtures thereof.

The copolymer is used in the emulsion in accordance with the invention in concentrations preferably ranging from 0.1 to 4% by weight and more particularly from 0.1 to 2% by weight relative to the total weight of the emulsion.

The emulsion of the invention is free of surfactant. Thus, on account of the absence of surfactant, this emulsion has the advantage of allowing the incorporation of heat-sensitive active agents and of not being irritant to the skin, particularly to sensitive skin.

Moreover, the average size of the globules in the oily phase, measured on a number basis by a laser scattering method, is less than 20 microns, and preferably ranges from 0.5 to 15 microns. On account of the fineness of these oil globules, the emulsion obtained has particularly satisfactory sensory and visual qualities.

The nature of the oily phase in the emulsion according to the invention is not critical. The oily phase can thus consist of any fatty substance, and in particular oils, conventionally used in cosmetics and dermatology.

Among the oils which can be used in the emulsion of the invention, mention may be made in particular, for example, of plant oils (jojoba oil, avocado oil), mineral oils (petroleum jelly), synthetic oils (ethylhexyl palmitate, isopropyl myristate), volatile silicone oils (cyclomethicone), non-volatile silicone oils and fluoro oils. The other fatty substances which can be present in the oily phase may be, for example, fatty acids, fatty alcohols and waxes (liquid jojoba wax).

The oily phase of the emulsion can represent from 15 to 45% by weight and better still from 20 to 30% by weight relative to the total weight of the emulsion.

The emulsion according to the invention can be used in any field in which this type of pharmaceutical form is advantageous, in particular in cosmetics and dermatology. When it constitutes a cosmetic and/or dermatological composition, it also advantageously contains a physiologically acceptable medium, i.e. a medium which is compatible with the skin, mucous membranes, the nails and/or the hair.

The emulsions which are the subject of the invention find their application in a great number of cosmetic and/or dermatological treatments for the skin, mucous membranes and the hair, including the scalp, in particular for protecting, caring for, cleansing and/or making up the skin and/or mucous membranes, for protecting, caring for and/or cleansing the hair and/or for therapeutically treating the skin, the hair and/or mucous membranes (the lips).

The emulsions according to the invention can be used, for example, as care products and/or cleansing products for the face in the form of creams or milks, or as make-up products (for the skin and lips) by incorporation of fillers, pigments or dyes.

Thus, a further subject of the invention is the cosmetic use of the emulsion as defined above for

treating, protecting, caring for and/or cleansing the skin, mucous membranes and/or the hair, and/or for making up the skin and/or mucous membranes.

Another subject of the invention is the use of the emulsion as defined above for manufacturing a dermatological composition intended for treating and/or protecting the skin, mucous membranes and/or the hair.

In addition, in a known manner, the emulsions of the invention can contain adjuvants that are common in cosmetics or dermatology, such a hydrophilic or lipophilic active agents, preserving agents, antioxidants, fragrances, solvents, fillers, screening agents, dyestuffs, basic agents (triethanolamine) or acidic agents, as well as lipid vesicles. These adjuvants are used in proportions that are usual in cosmetics or dermatology, and, for example, from 0.01 to 30% relative to the total weight of the emulsion, and they are, depending on their nature, introduced into the aqueous phase or into the oily phase of the emulsion, or alternatively into vesicles. These adjuvants and their concentrations must be such that they do not modify the property desired for the emulsion.

If it is desired to obtain a less fluid emulsion, one or more gelling agents can be added thereto, such as clays, polysaccharide gums (xanthan gum), carboxyvinyl polymers or carbomers. These gelling agents are used in concentrations ranging from 0.1 to

10%, preferably 0.1 to 5% and better still from 0.1 to 3% relative to the total weight of the composition.

The emulsions of the invention can optionally be free of solvent. This is also in keeping with a relatively non-aggressive and non-irritant emulsion which can be used by individuals with sensitive skin. However, if necessary, they can contain a solvent, in particular a lower alcohol containing from 1 to 6 carbon atoms, more particularly ethanol. The amount of solvent can range up to 30% relative to the total weight of the composition.

The emulsions according to the invention can be prepared by any appropriate means for obtaining oily globules less than 20 microns in size. According to one preferred embodiment of the invention, they are prepared by using a microporous membrane, this technique making it possible to obtain a globule size which is particularly suited to the aim of the invention, and in particular calibrated, monodisperse oil globules. Such a technique is described, for example, in document EP-A-546 174.

Thus, a further subject of the invention is a process for manufacturing the emulsion as defined above, which consists in introducing, under pressure, the oily phase into the aqueous phase containing the copolymer, through a hydrophilic porous glass membrane with an average pore size ranging from 0.1 to 5 μm and

preferably from 0.3 to 3 μm, at a pressure greater than the critical pressure.

Preferably, the membrane is pretreated under vacuum and with ultrasound in demineralized water containing about 2 grams per litre of aqueous phase of the composition according to the invention, this treatment lasting for about 1 hour.

The expression "critical pressure" means the minimum pressure required to introduce a dispersed phase into a continuous phase through a porous glass membrane of determined pore size. The critical pressure (in kPa) is defined by the following equation:

$Pc = 4\gamma_{ow}\cos\theta/D_m$,

in which γ_{ow} is the interface tension (mN/m), θ is the contact angle (rad) and D_m is the average size of the pores (μm) of the porous glass membrane.

In the process of the invention, the pressure used is preferably Pc + 20 kPa.

For example, a membrane with a pore size ranging from 0.1 to 5 μm can be used, using a pressure preferably ranging from 350 to 30 kPa (3.5 to 0.3 bar). Preferably, the membrane used has a pore size of 0.3 μm, 0.7 μm or 2.8 μm and, in this case, a pressure ranging, respectively, from 220 to 320 kPa (2.2. to 3.2 bar), from 140 to 200 kPa (1.4 to 2 bar) and from 30 to 70 kPa (0.3 to 0.7 bar) is used.

The example below illustrates the invention. In this example, the percentages are given on a weight basis.

Example 1:

Phase A

Pemulen TR2		0.75	%
Triethanolamine		0.75	%
Preserving agents		0.2	%
Demineralized water	qs	100	%

Phase B

Volatile silicone oil (cyclopentasiloxane)	20	%

Procedure:

A membrane with a pore size of 0.7 µm is immersed in one litre of demineralized water containing 2 grams of phase A, and is then placed under vacuum and under ultrasound for one hour.

After this treatment of the membrane, phase A is pumped to pass it into the membrane. Phase B is placed under pressure up to the critical pressure of 170 kPa (1.7 bar). Phase B is then emulsified in phase A under a pressure of 190 kPa (1.9 bar).

A very fine emulsion is obtained which feels very pleasant when applied.